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Mineral Processing Laboratory

January 1988

Project 3.0.2.9.01
Advance Ceramic Materials

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15 pp

MINERAL SCIENCES LABORATORIES
DIVISION REPORT MSL 88-9 (IR)

MICROMEDIA

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ABSTRACT

In this study, a laboratory autoclave was used to synthesize zirconia powder by reacting zirconium oxychloride with water or aqueous urea under elevated pressure-temperature (hydrothermal) conditions. Fine monoclinic zirconia powders are obtained at a temperature of 200°C and a pressure of about 1.5 MPa. X-ray diffraction and scanning electron microscopy were used to characterize the crystalline phase and the particle sizes measured by sedigraph. The results indicate that aqueous urea produces ultra fine, well crystallized powder.

Keywords: Hydrothermal processing; zirconia; urea-zirconium oxychloride reaction; fine powder.

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POUDRE DE ZIRCONE SYNTHÉTISÉE HYDROTHERMIQUEMENT- ÉTUDE PRÉLIMINAIRE

par

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RÉSUMÉ

Pour les besoins de cette étude, nous avons utilisé un autoclave de laboratoire pour synthétiser de la poudre de zircone en faisant réagir de l'oxychlorure de zircone avec de l'eau ou de l'urée aqueuse dans des conditions hydrothermiques (température et pression élevées). De fines poudres monocliniques de zircone ont été obtenues à une température de 200°C et à une pression d'environ 1,5 MPa. Les techniques de diffraction des rayons X et de microscopie électronique à balayage ont été utilisées pour caractériser la phase cristalline et la dimension des particules mesurées au moyen de l'appareil "sedigraph". Les résultats indiquent que l'urée aqueuse permet d'obtenir une poudre ultra-fine et bien cristallisée.

Mots-clé : Traitement hydrothermique; zircone; urée-zirconium; réaction d'oxychlorures; poudre fine.

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INTRODUCTION

Structural ceramics are currently the focus of an intense international research and development program due to their potential applications in heat engines, cutting tools and other wear-resistant components. In view of this interest, CANMET has undertaken an in-house research program aimed at developing high-strength, wear-resistant materials. Zirconia has many physical characteristics which are of interest to ceramic engineers. These include strength, toughness, hardness, wear resistance and properties such as low thermal expansion and low thermal conductivity. Zirconia has three polymorphs - monoclinic, tetragonal and cubic. The monoclinic form is stable up to about 1000°C where it transforms into a tetragonal structure with an accompanying volume decrease (1). This volume change makes it impractical to sinter zirconia at high temperatures because the material tends to develop microcracks on cooling. The stability of the tetragonal modification is dependent on particle size, and extremely fine (<30 nm size) zirconia can exist in the tetragonal form at room temperature. The stabilization of the tetragonal form can also be accomplished by adding reagents such as MgO, CaO and rare-earth oxides to the zirconia (1,3). Since zirconia is one of the most promising structural ceramics, a study was carried out at CANMET to examine the feasibility of producing superfine ZrO_2 powders using the hydrothermal technique. This technique has emerged as an attractive alternative to the conventional and sol-gel processes because superfine powder can be produced at relatively low temperature and pressure (4-6). The optimum hydrothermal conditions for the synthesis of unstabilized zirconia powder are discussed in this report. The processing for stabilized zirconia powders will be presented in a future paper.

EXPERIMENTAL

Equipment

A Temp-Pres Research Hydrothermal System, model HR-2CC-1, was used in this study. The system consisted of:

(a) a two-temperature zone furnace,
(b) temperature controller,
(c) pressure vessel (autoclave), and
(d) a lift mechanism to raise or lower the autoclave into the furnace.

The temperatures of the two zones of the furnace were controlled independently by the proportional band and reset, and were monitored by chromel-alumel thermocouples.

A general schematic of the autoclave is shown in Fig. 1. The pressure vessel has a platinum liner with a capacity of 137 mL. The pressure generated within the closed system is dependent on the operating temperature and the volume % occupied by the solution (degreee of fill). It increases with both temperature and degree of fill.

Materials

The starting material was zirconium oxychloride which can have several states of hydration (7). The most common forms are $ZrOCl_2.8H_2O$ (containing 44.7% H_2O) and $ZrOCl_2.6H_2O$ (containing 37.7% H_2O). In order to determine the exact hydration state of the zirconium oxychloride used in this investigation, a weighed amount of this material was heated in a platinum crucible to 1000°C and maintained at this temperature for 30 minutes. The weight of the residue in the crucible was determined and a weight loss of 59.5% was recorded. The solid residue was identified by x-ray diffraction as monoclinic ZrO_2. This weight loss represented the loss of water and hydrogen chloride from the oxychloride molecule according to the equation:

$$ZrOCl_2.xH_2O \longrightarrow ZrO_2 + 2HCl + (x-1)\ H_2O \qquad (1)$$

In addition, thermogravimetric analysis (TGA) was used to further determine the thermal behaviour of the zirconium oxychloride. The results are presented in Fig. 2 and show that the thermal decomposition of the material involves two distinct steps. The slope of the weight loss versus temperature curve changes sharply at about 190°C corresponding to a weight loss of about 41%, indicating a change in the reaction rate; a total weight loss of 59% is recorded at 760°C. This total agrees well with the value of 59.5% obtained by heating the material to 1000°C. Below 200°C, the weight loss can be ascribed to dehydration of the oxychloride to the monohydrate according to the equation:

$$ZrOCl_2.xH_2O \longrightarrow ZrOCl_2.H_2O + (x-1)\ H_2O \qquad (2)$$

and above the 200°C to dehydrochlorination according to:

$$ZrOCl_2.H_2O \longrightarrow ZrO_2 + 2HCl \qquad (3)$$

The results show that the material under investigation corresponds closely to $ZrOCl_2.7H_2O$, and it could be a mixture of the two common forms, $ZrOCl_2.8H_2O$ and $ZrOCl_2.6H_2O$.

Preparation of Zirconia

A weighed amount of zirconium oxychloride is dissolved in 75 mL of hot distilled water; the solution is cooled and calculated amounts of urea are added; the solution is diluted to 110 mL and transferred to the autoclave to make 80% fill. In some experiments, urea was not included.

To ensure safety, the autoclave must be properly sealed to withstand both temperature and pressure by carrying out the following steps: place platinum liner cap over the platinum liner; assemble the plunger, sealing gasket, back-up gasket, and thrust washer and place them in the vessel throat (Fig. 1); clean and lubricate all threads on the vessel and cap nut

with high temperature lubricant (Molybdenum grease); tighten the cap with a torque wrench at 165 N.m.; place the flat washer and extraction nut on the plunger.

The autoclave was then lowered into the furnace. The temperature chosen for the present work was 200°C and the estimated pressure generated at 80% fill was 1.5 MPa. The residency time of the solution in the autoclave varied from 8 to 24 hours. Upon completion of the experimental run, the autoclave was cooled to room temperature, and disassembled. The slurry was removed from the autoclave and the pH was measured. The precipitate was washed repeatedly with distilled water to remove the chloride and finally isopropyl alcohol was added to the precipitate and then dried in a rotary vacuum evaporator. Final drying of the powder was accomplished in an oven at 120°C.

The dried powders were characterized by X-ray diffraction (XRD) (for phase content), scanning electron microscopy (SEM) and sedigraph (for morphology and particle size).

RESULTS AND DISCUSSION

The experimental conditions and results of the hydrothermal synthesis of zirconia are summarized in Table I. The results clearly indicate that the particle size of powders derived from urea-containing solutions is finer than those without urea, suggesting that urea influences the nucleation and growth of the product crystals. The hydrolytic reaction producing zirconia from zirconyl chloride may be represented by the reversible equation:

$$ZrOCl_2 + H_2O \rightleftharpoons ZrO_2 + 2HCl \qquad (4)$$

The hydrolysis of urea produces ammonia which in turn neutralizes the HCl produced in reaction (4), thereby promoting the forward reaction also. The hydrolysis is represented by the equation :

$$CO(NH_2)_2 + H_2O \longrightarrow CO_2 + 2NH_3 \qquad (5)$$

The hydrolysis is slow at room temperature, but accelerates at higher temperatures (8). The precipitation is therefore controlled by temperature and duration of heating. In this study, the solution was heated to 200°C, and at this temperature the rate of hydrolysis reaction should be very high and consequently a large number of zirconia nucleation sites should be formed in the solution, resulting in fine zirconia.

The particle size analysis results show that, in general, longer time produces finer powder with the exception of the results for samples 4 and 5. The finest powders were obtained from samples 8, 10 and 11 which were precipitated from a slurry with pH=10. The effects of reaction time and the pH of the slurry on the crystallization of the zirconia are not clear and need further examination.

The morphological characteristics of the dried powders were examined by scanning electron microscopy. A Photomicrograph of the as-prepared, rotary evaporator-dried powder is shown in Fig. 3. No recognizable morphological characteristics are present in the material and this is due to the agglomeration of fine particles. The as-prepared spray-dried powder sample 6 (Fig. 4) formed spherical aggregates with sizes varying from 1 to 8 μm. These spheres are suspected to be hollow because they floated in water during particle size measurements by sedigraph, making the size analysis impossible. The development of the hollow spheres after spray-drying made it difficult to form dense bodies by sintering.

X-ray diffraction results showed that monoclinic ZrO_2 was the only phase present in the product. Very diffuse diffraction lines were obtained for powders prepared without urea showing that the material was very poorly crystallized in these cases. With urea, however, sharper patterns were obtained. These results indicate that fine crystallized zirconia powder can be obtained from solutions containing urea.

CONCLUSION

The synthesis of exceptionally fine powders of monoclinic zirconia has been achieved by a hydrothermal process using zirconyl chloride and urea. The process is carried out at a temperature of 200°C and a pressure of about 1.5 MPa. The effect of the urea in solution is to increase the number of nucleation sites thereby producing fine well-crystallized ZrO_2. Monoclinic ZrO_2 is the only phase observed in the hydrothermally synthesized powder.

As the second part of this project, MgO or Y_2O_3 partially stabilized zirconia (psz) will be synthesized in the hydrothermal system. These PSZ powders will be used to produce zirconia toughened mullite ceramics.

ACKOWLEDGEMENT

The authors wish to thank Dr. S. Mikhail of the Physical Chemistry Section for performing the TGA and D. Owens of the Mineralogy Section for doing the SEM work. Thanks are also due to Bell Northern Research for donating the hydrothermal equipment used for this work.

REFERENCES

1. Burkin, A.R., Saricimen, H. and Steel, B.C.H. "Preparation of yttria stabilized zirconia (YSZ) powders by high temperature hydrolysis (HTH)"; Trans J Brit Ceram Soc 79:105-108; 1980.

2. Garvie, R.C. "Occurrence of metastable tetragonal zirconia as a crystallite size effect"; J Phys Chem; 69:4 1238-43; 1965.

3. Haberko, K. and Pyda, W. "Preparation of Ca-stabilized ZrO_2 micropowders by a hydrothermal method"; Science and Technology of Zirconia II, Advances in Ceramics 12:774-783; Am Ceram Soc; 1984.

4. Anon, "Commercialization of hydrothermal technique for producing superfine zirconia"; Techno Japan 19:9 67-68; 1986.

5. Tani, E., Yoshimura, M. and Somiya, S. "Formation of ultra-fine tetragonal ZrO_2 powders under hydrothermal conditions"; J Am Ceram Soc 66:1:11-14; 1983.

6. Tani, E. Yoshimura, M. and Somiya, S. "Hydrothermal preparation of ultrafine monoclinic ZrO_2 powders"; J Am Ceram Soc 64:12:c-181; 1981.

7. Blumenthal, W.B. "The chemical behaviour of zirconium"; Princeton, N.J., D. Van Nostrand Co; 1958.

8. Day, R.A. Jr and Underwood, A.L. "Quantitative analysis"; Tokyo, Maruzen; 1959.

Table I. Effect of experimental conditions on pH of the slurry and particle size of powders

Sample no.	Wt. of urea, g	Wt. of zirconium oxychloride, g	Reaction time, h	pH of slurry	Particles % <1 μm	<0.2μm
1	13.6	31.7	48	11	85	58
2	13.6	31.7	24	11	76	65
3	13.6	31.7	8	11	56	47
10	10.8	35.1	48	10	95	72
8	10.8	35.1	24	10	88	67
11	10.8	35.1	8	10	83	61
4	6.9	36.2	48	2	58	48
5	6.9	36.2	24	2	84	62
6	6.9	36.2	8	2	n.d.	n.d.
12	0	40.0	48	0	27	17
7	0	40.0	24	0	9	2

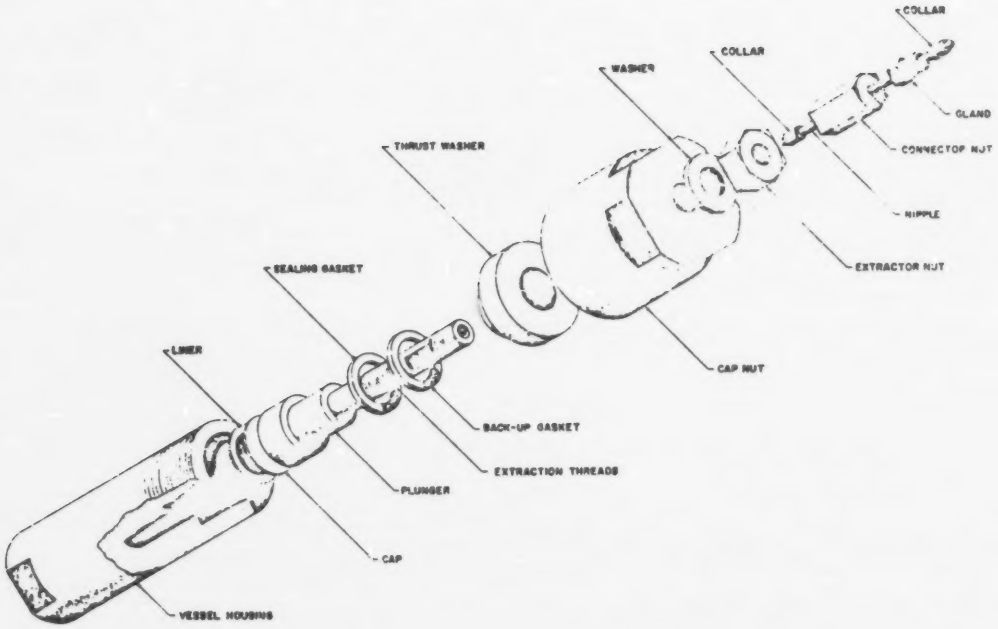

Fig. 1 – Pressure vessel assembly

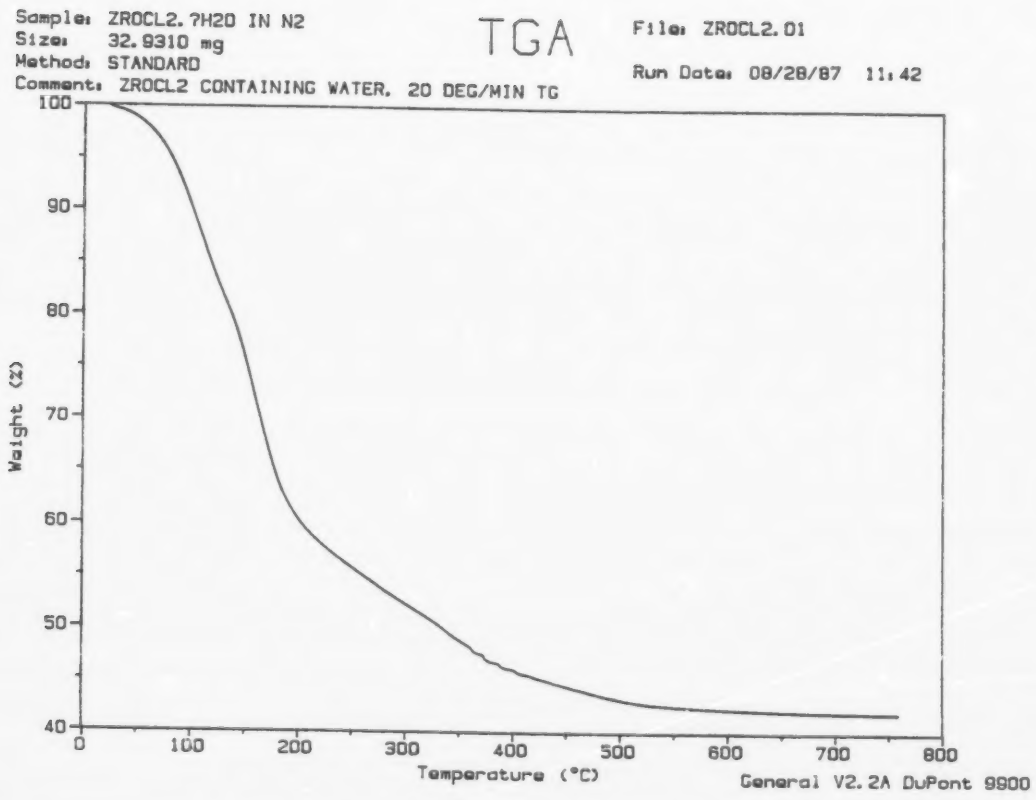

Fig. 2 - TGA curve for zirconium oxychloride

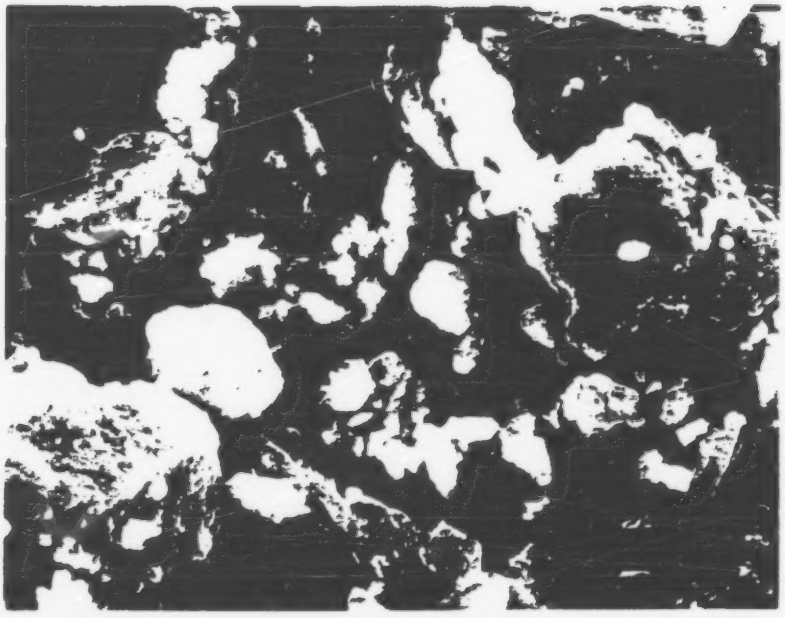

Fig. 3 - SEM micrograph of a rotary evaporator dried powder

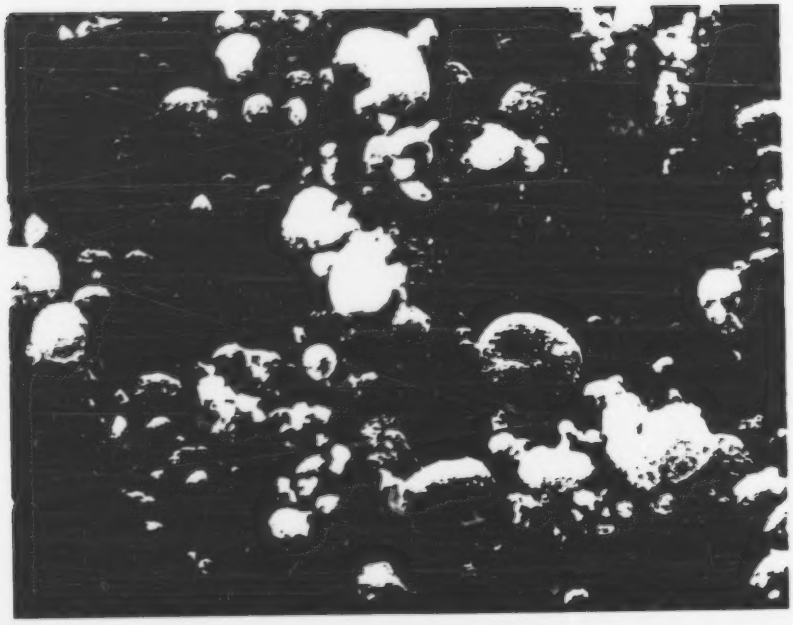

Fig. 4 - SEM micrograph of a spray-dried powder